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X-ray Fluorescence in the IAEA and its Member States

In This Issue

Activities in the IAEA XRF Laboratory

A few selected examples of the recent activities and results in the field of XRF are presented.

In-situ analysis of bronzes by portable X-ray fluorescence spectrometry

The performance of a portable XRF spectrometer, when applied for quantitative analysis of bronze samples, has been tested. The spectrometer has been constructed and manufactured in the Instrumentation Unit, the IAEA Laboratories, Seibersdorf, Austria. It consists of an air-cooled low-power (50W), Pd-anode X-ray tube. The X-ray spectra were acquired with a Si-PIN detector. The detector energy resolution, FWHM, was 210 eV at 5.9 keV, the detector active area was 7 mm^2, and the Be-window thickness 12.7 micrometers. All measurements were carried out in air in direct excitation geometry. A rhodium 100 µm thick filter was inserted between the tube window and the sample. The tube was operated at 45kV and the current between 0.2-1.0 mA was applied. The measuring time varied form 200 s to 1000 s per sample. The diameter of the irradiated area was about 5 mm.

Two groups of samples were analysed: standard reference materials (NBS 1103, NBS 1108, NBS 1115) and selected points on a bronze horse statue. The standards were measured in a sample holder installed on a detachable table. For the measurements of the horse statue the table was removed and the spectrometer was positioned in front of the horse.

Fig. 1. The portable XRF spectrometer performing the analysis of a horse statue. In the left lower corner a close-up of the excitation geometry is shown.

For precise adjustment of the tube-sample-detector geometry two laser pointers were used. The spectrometer performing the analysis of the horse statue is shown in Fig. 1. For the quantitative analysis the spectrometer has been calibrated with a set of pure-element calibration standards (thick metal foils and simple chemical compounds, pelletized, if necessary with addition of binder). In order to obtain the net peak areas the collected X ray spectra were processed by spectra fitting software. Strong overlap between the Ni-Kα and Cu-Kα peaks was observed which limited the accuracy of analysis for the samples containing < 0.5% of Ni. A fundamental parameter method was used to calculate the element concentrations in the analyzed samples. The absorption and enhancement effects were corrected. The calculated concentrations of elements were normalized to 100 %. The determined concentrations of elements in the bronze horse statue are shown in Table 1. Table 2 contains the results for the NBS 1103 SRM, Tables 3-4 contain the results for the other two NBS reference standards, together with the values obtained with standalone energy dispersive XRF laboratory system with polarized targets.

Table 1. Concentrations of elements in four different spots on a horse statue obtained with portable XRF spectrometer during in-situ analysis.

Ele-ments	Spot 1	Spot 2	Spot 3	Spot 4
	[wt. %]	[wt. %]	[wt. %]	[wt. %]
Cu	88.23*	89.72	90.82	90.44
Zn	3.81	3.54	3.64	2.87
Sn	6.5	5.3	4.3	5.6
Pb	0.70	0.61	0.48	0.25
Fe	0.10	0.08	0.09	0.1
Ni	0.7	0.7	0.7	0.8

*uncertainty of the results due to counting statistics is not greater than the last significant figure.

Table 2. Concentrations of elements in standard NBS 1103.

Elements in NBS 1103	Certified values	Values obtained at the IAEA with portable XRF
	[wt. %]	[wt. %]
Cu	59.27*	59.46
Zn	35.72	36.93
Fe	0.26	0.31
Ni	0.15	0.4
Pb	3.21	2.34

*uncertainty of the results due to counting statistics is not greater than the last significant figure.

Table 3. Concentrations of elements in standard NBS 1108

Elements in NBS 1108	Certified values1)	Values obtained with standalone, polarizing targets XRF spectrometer2)	Values obtained with portable XRF2)
	[wt. %]	[wt. %]	[wt. %]
Cu	64.9_5	67.98	63.73
Zn	34.4_2	33.79	36.06
Pb	0.063	0.065	0.10
Fe	0.050	0.09	0.11
Sn	00.39	0.394	0.9
Ni	0.033	0.073	0.2
Mn	0.025	0.029	-

1) Uncertainty of the result is not greater than ± 1 in the last significant figure, except for a subscripted value for which it is not greater than ± 5.
2) Uncertainty of the result due to counting statistics is not greater than the last significant figure.

Table 4. Concentrations of elements in standard NBS 1115.

Elements in NBS 1115	Certified values1)	Values obtained with standalone, polarizing targets XRF spectrometer2)	Values obtained with portable XRF2)
	[wt. %]	[wt. %]	[wt. %]
Cu	87.9_6	90.74	86.76
Zn	11.7_3	11.37	12.76
Fe	0.13	0.176	0.16
Sn	0.10	0.097	-
Ni	0.074	0.133	0.3
Pb	0.013	0.013	0.07
P	0.005	DL (0.002)	-

1) Uncertainty of the result is not greater than ± 1 in the last significant figure, except for a subscripted value for which it is not greater than ± 5.
2) Uncertainty of the result due to counting statistics is not greater than the last significant figure.

As can be noticed the quality of the results obtained with the portable and standalone XRF systems is comparable, especially for the major and minor components. The observed differences are more significant for low-abundance components like Pb, Fe, Sn, Ni, Mn. This is due to spectral interferences (Fe, Mn, Ni) and also due to higher detection limits (Sn, Pb) of the portable XRF spectrometer as compared to the polarized targets XRF system.

It can be concluded that the portable XRF spectrometry is suitable for quantitative in-situ analysis of bronze objects for major elements and for semi-quantitative/qualitative analysis of minor and trace elements. The way for improving the results is by the use of more suitable, faster X-ray detector with a better energy resolution. For the determination of low-Z elements (P, Si but also Sn-Lα) a helium flash or shortening the air path would be required. These modifications are being introduced into the portable XRF system.

Acknowledgements

This work has been performed by staff of the XRF Group, IAEA Laboratories at Seibersdorf in collaboration with Prof. Peter Wobrauschek and Prof. Christina Streli from the Atominstitut, Vienna, Austria in the framework of the BRONZART project.

Micro-beam X-ray absorption and fluorescence measurement with synchrotron radiation – preliminary results

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The XRF Group of the PCI Laboratory provided the instrumentation for performing the measurements at the synchrotron beam line. The micro-beam X-ray scanning spectrometer was moved out from the Instrumentation Unit's XRF laboratory and was installed at the synchrotron beam line. The spectrometer was equipped with three X-ray detectors, namely: a large area silicon drift detector (active area of 50 mm2, positioned in the synchrotron orbital plane at 90 degrees in relation to the primary beam; the detector was provided by the Atominstitut, Vienna), for collecting the X-ray fluorescence spectra during elemental mapping and tomographic scanning; small area silicon drift detector (active area 2 mm2, positioned in the beam behind the sample), for collecting X-rays transmitted through the sample; and a silicon drift detector (active area of 10 mm2) fitted with a polycapillary half-lens and aligned in confocal geometry. The analyzed samples were mounted on a motorized xyzθ stage. The synchrotron beam was monitored with an ionization chamber and Si-PIN diode detectors. The scanning was controlled by a SPECTOR/LOCATOR data acquisition system. The overall view of the set-up installed at the ANKA synchrotron beamline is presented in Fig. 1.

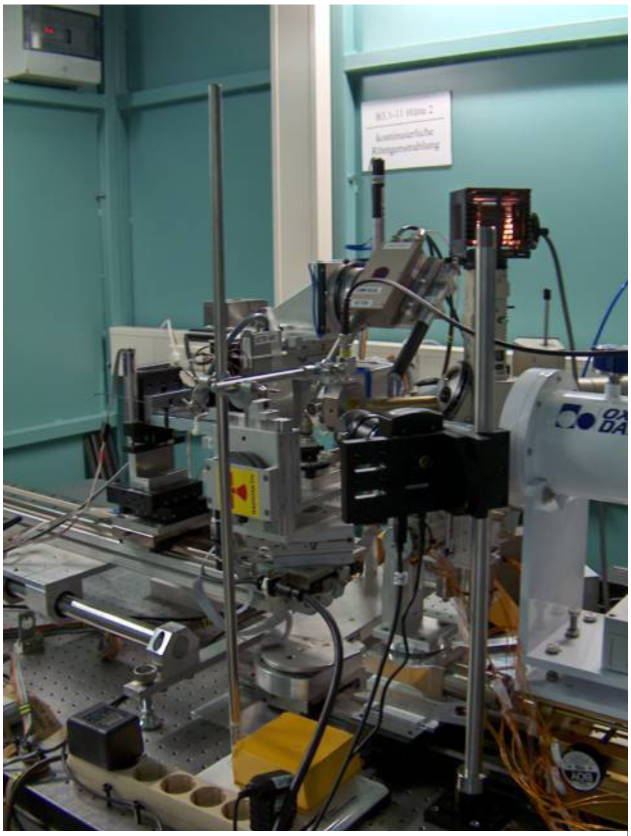


Fig. 1. The micro-beam X-ray fluorescence/absorption spectrometer installed at the ANKA synchrotron source.

Four groups of samples were analyzed by performing 2D/3D tomographic scanning in absorption/fluorescence mode and in a 3D confocal mode:

Freeze-dried human-bone sections prepared at the Atominstitut, Vienna, Austria in collaboration with the Instrumentation Unit.

U/Pu-rich particles provided by the Institute for Transuranium Elements, Karlsruhe, Germany.

Stained organs of malaria mosquitoes obtained from the Entomology Unit of the IAEA Laboratories and prepared using different methodologies by the Instrumentation Unit.

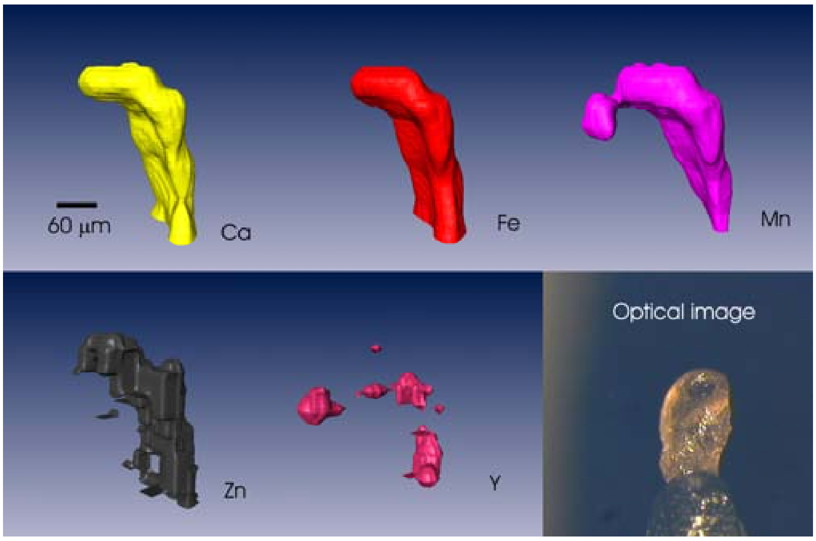
Mineral grain sample prepared by the Agency's fellow.

In the bone samples the distribution of lead was investigated by using 2D X-ray fluorescence tomography. For the U/Pu-rich particles the 2D/3D elemental distribution maps were measured. The selected mosquito's parts were measured in 2D and 3D X-ray fluorescence tomography mode in order to reconstruct the morphological details of their organs in support of the Sterile Insects Technology (SIT) studies. Mr. Bielewski (Poland), the Agency's fellow performed a confocal imaging of elemental distribution in Fe/Ti-rich mineral grain. The aim of this measurement was to look for micro-heterogeneity of minerals.

Several additional measurements on standard samples were performed in order to establish the geometry of the synchrotron beam and other analytical parameters. The Instrumentation Unit is collaborating with the other groups on elaborating the acquired data.

In Fig. 2 the reconstructed distribution of Ca, Mn, Fe, Zn, and Y in mineral grain is presented. These results were obtained by confocal scanning. The results indicated that the major elements such as Ca, Fe, as well as Zn are evenly distributed within the grain. The manganese and especially yttrium show more heterogeneous distribution. Such observation is helpful in the interpretation of the results of quantitative analysis of individual mineral grains obtained from X-ray tube experiments. It enables for proper identification of the minor/trace elements that are the most suitable for classification of mineral grains using the results of the X-ray fluorescence analysis.

Fig. 2. Distribution of Ca, Fe, Mn, Zn and Y in a mineral grain (garnet). An optical microscopic image of the grain is shown in the bottom right.



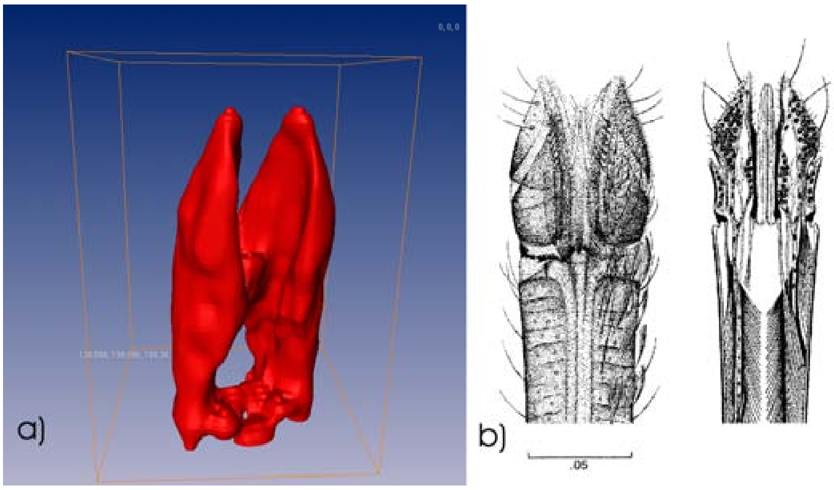


Fig. 3. Probocsis of a female mosquito (Anopheles), tomographic reconstruction (a), anatomical drawing (b – Aedes aegypti, from Jobling, Boris and David James Lewis, Anatomical Drawings of biting flies, British Museum of Natural History, London, in association with the Wellcome Trust, 1987)

In Fig. 3a a tomographic reconstruction of a proboscis of a female mosquito (Anopheles) is shown. For comparison, an anatomical drawing of the proboscis is shown in Fig. 3b. The reconstruction was obtained using the U-Lα radiation emitted from uranyl, which was used to stain the mosquito. Further work is being carried out at the Instrumentation Unit in order to develop methodology for staining different organs of mosquito with different heavy metals and to utilize the micro-beam X-ray fluorescence tomography to reconstruct their morphological details. The results of the lead in bone studies and U/Pu-rich particles are being evaluated in the collaborating institutions.

We would like to emphasize that the use of advanced analytical techniques in combination with synchrotron radiation source provided essential information about the investigated samples, which could not be obtained by other means. In particular, the use of the polarized and monochromatized synchrotron radiation dramatically improved the detection limits enabling X-ray fluorescence tomographic measurements of trace element distribution in bone tissue, mosquito samples and 3D mapping of element distributions in individual radioactive particles. The tasks were performed in cooperation with other research groups addressing the needs of the Member States laboratories. It should be a recommended way of bringing the Agency's support and expertise in applications of advanced nuclear analytical techniques directly to its Member States.

Support to Technical Cooperation projects

The XRF Group at Seibersdorf provides assistance to a number of Technical Cooperation (TC) projects where XRF is used as one of the analytical techniques. In 2005 some new regional TC projects were initiated and staff of the XRF Group contributed to organisation of planning/coordination meetings. The following meetings were held in 2005:

Planning Meeting for Nuclear Techniques for the Protection of Cultural Heritage Artefacts in the Mediterranean Region (RER/1/006), Vienna, 7-9 February 2005

The purpose of the meeting attended by the scientists and experts from Albania, Croatia, Cyprus, Greece, Malta, Serbia & Montenegro, Slovenia, TFYR Macedonia, Turkey, Belgium, France and IAEA staff was to present current status of applications of nuclear and related techniques in support of study and conservation of cultural heritage artefacts as well as to identify the national needs and regional priorities in the relevant field. The meeting agreed on the detailed work plan for 2005-2007 and recommended establishing in each country a national team consisting of analytical chemists and conservators as prerequisite for successful implementation of the project. Liaison with other relevant activities carried out under different international projects was also considered. The first regional activity under RER/1/006 will be a regional training course on research methodology for documentation, scientific investigation and preventive conservation of cultural heritage artefacts in the Mediterranean Region to be held in Malta in September 2005.

Planning Meeting for Air Pollution Monitoring in the Mediterranean Region (RER/8/009), Vienna, 28 February – 3 March 2005

The meeting was attended by the scientists and experts from Albania, Bosnia & Herzegovina, Croatia, Cyprus, Greece, Malta, Serbia & Montenegro, Slovenia, TFYR Macedonia, Turkey, Belgium, Germany and IAEA staff. A major purpose was to review the air pollution monitoring activities (including monitoring of heavy metals and radionuclides), available facilities and analytical procedures applied in the participating countries. Based on the needs and priorities of the countries the detailed work plan for 2005-2007 was established. One of the expected outputs is a network of the project counterparts and end-users to present the collected data in a standard way, and share the data among the participating countries. The first activity under RER/8/009 has been a regional training course on heavy metals monitoring held in Croatia in May 2005.

First Coordination Meeting of the Regional Project RLA/7/011 (ARCAL LXXX) on Assessment of Atmospheric Pollution by Particles, Buenos Aires, Argentina, 7-11 March 2005

The meeting was attended by the project counterparts from Argentina, Chile, Cuba, Mexico, Uruguay, Venezuela, expert from USA and IAEA staff. A major purpose of the meeting was to define a baseline for the project (by considering current activities and facilities available in the participating countries), to identify the needs and priorities, and to finalise the detailed work plan for 2005-2006. An active involvement of end-users from the beginning of the project and intake of the analytical data generated through the project by the end-user institutions were recommended. Moreover, the modalities to strengthen Technical Cooperation between the Developing Countries, and the actions to ensure sustainability of the project activities were identified. The first activity under RLA/7/011 will be a regional training course on sampling and black carbon determination to be held in Uruguay in July 2005.

Executive Meeting on Air Pollution Related to Transboundary Effects, Visibility, Climate Change and Agriculture (RAS/7/013), Sydney, Australia, 5-7 April 2005

The meeting was attended by the participants from Australia, Bangladesh, New Zealand, Philippines, Thailand, USA, Asian Development Bank and IAEA staff. A major purpose of the meeting was to review the effects of air pollution (in particular air particular matter) on transboundary movement, visibility, climate change, human health and agriculture, and to discuss possible role of the nuclear analytical techniques (NATs) in support of air pollution monitoring and air quality management (AQM). Moreover, the regional priorities in the field of AQM were identified along with a possible response under IAEA-sponsored TC projects. The meeting concluded that the NATs can provide valuable analytical data to enable source identification and source apportionment as well as to support ecotoxicology studies that are essential for assessment of toxicity and fate of pollutants in environment. Possible future activities under new regional initiatives (including TC projects) were also identified.

Further information on support to TC projects is available from Andrzej Markowicz (A.Markowicz@iaea.org).

5th International BioPIXE Symposium

The 5th International BioPIXE Symposium took place at Wellington, New Zealand, from the 17th – 21st January 2005. Oral and poster presentations were made covering topics in Biological Sciences; Environmental Sciences; Agricultural and Ecological Sciences; and Biomedical Sciences and Applications. There were fifty-three (53) participants from sixteen countries who took part in the Symposium and there was an exhibition mounted by commercial companies dealing with PIXE-related equipment and accessories. The theme for the Symposium was “Broad beam meets microprobe for bio-environmental R&D.”

The following key issues were highlighted during the symposium:

1. Aerosol Studies

Macrobeam PIXE has been used in aerosol studies mostly for elemental analysis of bulk aerosol samples, while microbeam PIXE analysis is used for single aerosol particle analysis. Even though both produce trace element concentration results, microbeam analysis is superior for source identification of pollutants. More useful information is derived from aerosol analysis data when additional statistical analysis is carried out to enable pollution source identification, source apportionment, and pollution management. Radioactive aerosol monitoring for short-lived and long-lived radioisotopes that exit in nature or generated by nuclear explosions also complement information needed in understanding and improving atmospheric transport models. An interesting development also reported at the Symposium is the use of both macro- and microbeam PIXE for the analysis of atmospheric liquid aerosols (fog, and rain droplets).

2. Biological/Medical Applications

The determination of trace element concentrations in various organs of freshwater fish by PIXE, enables a study of their migrational history and their exposure to various environmental stresses such as heavy metal toxicity, radiation, and agricultural chemicals. Microbeam PIXE is also being used to study the efficacy of target-chemotherapy reagent directed by irradiation, through the analysis of Pt and Cu after low dose irradiation of carboplatin and alginate capsules.

The Clean Air Society of Australia and New Zealand (CASANZ) organized, concurrently on the 19th January 2005, a one-day workshop. The workshop was focused on air particulate matter research.

Details on the Symposium can be obtained at : http://www.gns.cri.nz/biopixe5/

The spreadsheet method for calculating uncertainty in total reflection X-ray fluorescence analysis.

Since publication of the "Guide to the expression of Uncertainty in Measurement" by ISO in 1993 there has been an always-increasing interest in its implementation in the every day analytical laboratory practice. Nevertheless, probably due to the complexity of this document and due to the variety of new concepts introduced, it had a difficult way towards the practical implementation. In 1995 the first edition of the EURACHEM Guide gave a strong impulse to this process. Especially the second edition of this Guide, led to a rapid incorporation of the standardized methods of uncertainty quantification.

The EURACHEM/CITAC Guide stresses the idea that once calculated for a given method in a particular laboratory the uncertainty estimate might be reliably applied to subsequent results obtained by the method in the same laboratory. Yet, the establishment of uncertainty requires a significant effort. Several computer programs have been developed to assist analytical laboratories in calculating uncertainty when the sources of uncertainty were identified.

In this frame an Excel® workbook that uses the spreadsheet method of calculating uncertainty for the total reflection X-ray fluorescence (TXRF) analysis of liquid samples was developed. It requires that at least three different-concentration solutions of the same elements, prepared out of single element standard solutions are measured for calibration (relative sensitivities determination). It is also assumed that no volumetric flasks, but micropipettes are used to prepare all needed solutions. The workbook allows for the internal standard element to be chosen and changed according to the needs of a particular analysis while the reliability of the calibration remains unchanged. It accepts as inputs the AXIL (from QXAS) generated results files. The user enters uncertainties of the volumes and reference solutions as standard deviations, and the program calculates expanded uncertainty and produces a detailed report for every element in the sample.

The program and the technical support in its use are freely available from the Instrumentation Unit of the Agency's Laboratories, Seibersdorf, Austria. Further information is available from Ernesto Chinea Cano (*E.Chinea-Cano@iaea.org*)

X-ray Fluorescence in Member States

During the last months we received contributions from Albania, Ghana, Kenya and Sri Lanka on the current XRF activities. Below there are communications based on the original submissions (with minor editorial changes only). Because of importance an extended communication from Kenya along with detailed results was included.

Albania

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The activities on Energy-Dispersive X-ray Fluorescence Laboratory at the Institute of Nuclear Physics (INP) in Tirana, Albania started about 30 years ago from using simple systems consisting of single channel analysers, radioisotope sources and gas proportional or scintillation counters along with balanced filters for the separation of analytical lines. These systems were applied for the determination of single elements. A few portable prototypes were developed and successfully used for the determination of chromium and copper in ores, both in the lab and in-situ (ore processing plants) conditions.

Later, through different TC projects with IAEA, the lab has been equipped with the following systems:

- X-ray tube excited EDXRF spectrometer with secondary target excitation
- Radioisotope excited EDXRF system
- TXRF module
- Field portable XRF system based on a Cd-109 disc source, Si-PIN detector and pocket MCA.

From the beginning our work has been focused on research, applications and training. Due to the fact that our EDXRF systems are made of different parts that are put together, our research activities are mainly related to optimization of excitation geometry and the development of optimized analytical procedures for the analysis of different group of elements in several kinds of samples. Some of these procedures include:

- Determination of major and minor elements in soils, sediments, mineral ores and different type of rocks
- Determination of sulphur and some trace elements (V, Ni, etc.) in oil, bitumen and asphaltene
- Determination of some trace metals in sea and surface waters
- Determination of elemental composition of aerosols loaded on filters
- Determination of some trace elements in biological samples.

An important point of our work is related with the quality of the analytical results. For this reason we have participated in some of the intercomparison runs organized by AQCS of the IAEA and in the GeoPT proficiency tests. In most cases our reported results have been in good accordance with the respective accepted or recommended values.

Based on the advantages of EDXRF and on the fact that our lab is the only one in the country using this analytical technique, our group has been involved in several research projects and applications in the fields of geology, geochemistry, environmental monitoring, archaeology, etc. Some of the projects carried out during the last years are summarized bellow:

- Geochemical mapping of Albania
- National monitoring program for water and air pollution
- Technological study of Illyrian terracotta of Aphrodite and related ceramics of Hellenistic period from Belesh, Albania
- Identification of inorganic pigments used in old Albanian icons by TXRF
- Assessment of copper pollution in over-bank sediments of Mati river by in-situ measurements using a FPXRF instrument
- Identification of late-Byzantine and post-Byzantine wall paintings' materials and technology in Albania; mutual influence between Albanian and Greek iconographers.
- The study of ancient silver coins minted by Illyrian king Monounios (3-d century BC) and their comparison with same type and period silver coins from the cities of Dyrrachion and Korkyra.

Lately, FPXRF system is being used for new in-situ applications like assessment of pollution of soils and sediments, and analysis of different cultural heritage objects (metals, stones, paintings).

Training is provided for the students of Physics, Chemistry and Geology at both undergraduate and postgraduate levels.

Ghana

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The XRF laboratory is one of the laboratories in the Physics Department of the National Nuclear Research Institute (NNRI) of Ghana Atomic Energy Commission (GAEC). The laboratory serves as an analytical laboratory among other things. The analytical work includes the analysis of vegetation, water, air and geological samples among others using both conventional XRF and TXRF techniques. The laboratory had been able to acquire basic equipment needed for its activities mostly through Technical Cooperation (TC) and Coordinated Research Project (CRP) with the IAEA. The research work is mostly done in collaboration with other institution/laboratories within and outside GAEC. Some of the institutions outside GAEC that we collaborate with are Tema Oil Refinery (TOR), Environmental Protection Agency (EPA) of Ghana, Ghana National Petroleum Corporation (GNPC), Universities, industries etc. and their needs are mainly in environmental pollution monitoring. The commercial work is done mostly for the industries, e.g., the metal and some food processing companies.

The laboratory for some years had been looking at Gold tailings in both Obuasi and Prestia gold mines in Ghana. Characterising the ore, tailings and tracing the path of the tailings in nearby rivers.

For the past five years, the laboratory had been involved in the Coordinated Research Project on Biomonitoriong of Trace Element Atmospheric Pollution. This project was to determine the suitability in the use of local Lichen for biomonitoring of air pollution in Ghana. This project has ended. The project involved the following areas:

- Carrying out a biomonitoring survey around some gold mining areas in Ghana using lichens as the biomonitors.
- Collecting aerosols at the same sampling sites using Gent samplers
- Analysing collected samples by XRF and NAA
- Analysing data by carrying out lichen mapping and source apportionment.
- Participating in Agency quality control exercises.

In 1999 the laboratory embarked on a TC project titled - Binational Environmental Monitoring and QC of the Tano Basin. This basin is common to both Ghana and Cote'de Ivoire. The project was therefore carried out in collaboration with the Laboratoire National de la Sante Publique (LSNP-Cote d'Ivoire). The project aimed at developing a common strategy and methodology for the effective environmental monitoring and quality control of activities in the Tano basin of both countries.

The laboratory was also involved in a CRP with the Agency on the "In-situ application of XRF" and we applied a Field Portable XRF System for analysing finish products and metal scrap sorting. This is to investigate the potentials of using portable XRF spectrometry to develop methods for effective characterisation of metal scrap for sorting, and analysis of the finish products for the steel industries using Mn/Fe elemental ratio.

The Government of Ghana has approved a Legislative Instrument banning the production, importation, storage, sale and use of leaded gasoline in the country with effect from 1st January 2004. Consequently, Methylcylopentadienyl Manganese Tricarbonyl (MMT), a manganese-based gasoline anti-knock additive has been in use in Ghana since January 2004 in unleaded gasoline production. Manganese is a natural component of soil and also an element that is essential to maintaining good health. However, prolonged periods of exposure to high levels of airborne manganese concentrations can cause adverse health effects. An environmental impact assessment and management plan for the use of the new additive is to be submitted to Ghana Environmental Protection Agency for approval.

The Tema Oil Refinery (TOR) Ltd. in collaboration with the Physics Department of the Ghana Atomic Energy Commission (GAEC) is now carrying-out an Air Quality Monitoring Programme. This programme will be partly sponsored by Afton Chemicals, the suppliers of MMT. They will provide funding for TOR personnel to receive training and also acquire dichotomous air monitoring equipment at Research Training Institute (RTI), U.S.A. The filters will initially be analysed by neutron activation analysis at the University of Montreal in Canada but subsequent ones will be analysed by the Ghana Atomic Energy Commission using both NAA and XRF facilities. The aim of the programme is:

1. To determine baseline concentrations of Manganese (Mn) in ambient air and soil in both urban and rural communities.
2. To comply with National EPA's environmental impact assessment regulations.
3. To build capacity through collaboration with internationally recognised experts and organizations in the area of air pollution monitoring.
4. To establish a framework for continuous monitoring of manganese in ambient air and soil using EDXRF and NAA.

The primary objectives of the "Manganese in air" project are:

- To evaluate concentrations of Manganese in air in urban and rural areas, and make an informed assessment of the potential adverse (if any) health effects.
- To determine Manganese levels in both PM2.5 and PM10 and make inferences concerning source such as soil, industrial, automobile/petroleum emissions.
- To generate the necessary data base for air quality modelling.

Kenya

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Trace element studies in traditional Kenyan diets

Introduction

Trace elements play an important role in human health because they participate in biological functions (Agget, 1985; Arlette and Charlotte, 2001) that contribute to growth and maintenance of life as well as good health. Excess or deficiency results in the failure of the biological function and the effect is exhibited in a variety of clinical disorders (Karl, 2002). Deficiency disorders are alleviated through supplementation whereas disorders due to excess levels are corrected by the reduction of excess amounts. Human beings obtain their trace elements mainly from food and water. Since they are required in small quantities, it is important to determine their concentration levels in these sources.

In Kenya, one of the most commonly consumed food is *ugali*; a semi-hard dish prepared from a mixture of maize flour and hot water that is cooked for approximately ten minutes. This is usually accompanied by a vegetable or fish relish. In this report, we present results on trace element levels in maize flour, kale vegetable and fish. In addition, some results on the trace element levels in tea, the most commonly consumed beverage, are reported.

Elemental content of maize flour and kale

The processing of maize reduces the elemental concentrations (Table 1), with potassium and zinc being the ones that are significantly reduced. The milling factor was observed in the pricing with most refined maize flour (Hostess) being the most expensive. The relatively high concentrations levels of calcium and iron in the *Jogoo* brand were probably caused by other factors not related to maize processing; possibly it is from contamination from the processing environment. In Table 2, the potassium and calcium levels in kale are observed to be several orders of magnitude higher than in the maize. It is also observed that the kale vegetable has high levels of manganese, iron, and zinc; therefore it is a good source of these essential elements. The concentration levels of the other elements in both foodstuffs are roughly in the same range.

Table 1. Mean value concentration (± 1 s.d.) in processed and unprocessed maize (μg/g)

Element	Processed maize meal			Unprocessed maize
	Hostess	Jogoo	Ugali	
K	1489 ± 299	1821 ± 163	2057 ± 166	3613 ± 60
Ca	26 ± 2	32 ± 3	43 ± 5	30 ± 1
Ti	1.7 ± 0.2	2.3 ± 0.6	2.9 ± 0.5	2.9 ± 0.3
Mn	1.9 ± 0.4	2.9 ± 0.4	3.3 ± 0.4	3.3 ± 0.3
Fe	19 ± 3	28 ± 6	39 ± 6	29.0 ± 0.3
Ni	0.6 ± 0.2	0.7 ± 0.2	0.5 ± 0.2	0.9 ± 0.4
Cu	0.9 ± 0.1	1.2 ± 0.2	1.0 ± 0.1	1.3 ± 0.4
Zn	7.0 ± 0.2	10 ± 2	13 ± 1	24 ± 3
Rb	1.9 ± 0.1	2.4 ± 0.7	2.3 ± 0.2	7.3 ± 0.3

s.d. is standard deviation

Table 2. Mean concentrations and range values in kale samples (µg/g) unless indicated otherwise)

Element	Mean	Range
K	2.95 ± 1%	2.20 – 4.20%
Ca	3.05 ± 0.7%	1.67 - 4.25%
Cr	3.27 ± 0.9	2.0 – 5.9
Mn	56.5 ± 28	30 – 105
Fe	93.7 ± 24	55 – 141
Cu	2.4 ± 0.9	1.5 – 4.2
Zn	96.5 ± 44	42.3 – 155
Br	< LLD (2)	LLD – 65
Rb	89.2 ± 24	50 – 129
Sr	107 ± 56	31.6 – 239

LLD is the lower limit of detection

Elemental content of tea and juices

Instant tea is a form of processed tea, which is in powder form. It is newly introduced and it is not yet a popular product. As shown in Table 3, there is quite a significant difference in the elemental concentration levels in this finely processed tea and in the usual tea leaves (Ketepa tea). In both cases, the manganese and iron concentration values are very high when compared to the values observed in maize and kale.

Table 3. Concentration levels (± 1 s.d.) in two brands of tea leaves (µg/g)

Element	Normal tea leaves	Instant tea leaves
K	16960 ± 3640	7234 ± 1601
Ca	3370± 399	403 ± 40
Ti	30 ± 9	< LLD (3.5)
Mn	1060 ± 169	3007 ± 80
Fe	345 ± 76	83 ± 20
Ni	3.5 ± 1.3	8 ± 1
Cu	13.5 ± 2.7	55 ± 3
Zn	3.1 ± 0.6	543 ± 15
Rb	116 ± 26	4 ± 1
Sr	42 ± 8	< LLD (3.5)

Elemental content in fish

Lake Victoria is the major source of fish that is consumed in the major towns of Kenya, including the City of Nairobi. Some of the fish is also exported to Europe. Surveillance and assessment of trace metals and other pollutant levels in the fish is important to ensure compliance with stipulated standards for human consumption. Non-compliance would lead to adverse health effects on the consumers as well as a ban on our fish at the foreign markets. The implication of a ban may adversely affect the economy of our country considering that currently the export earnings from this industry is 65 million US Dollar per annum. The fishing industry is also a source of employment and a revenue earner to the central government. Therefore, it is important to study the heavy metal levels in this aquatic environment. We report the elemental content of fish from Lake Victoria, in particular the *Lates niloticus,* which is the major fish species in the lake.

It is observed (see Table 4) that in general the liver accumulates the highest amounts of heavy metals, in particular iron and copper with values of 41.2 ± 7.9 and 0.81 ± 0.05 respectively. Lead, a non-essential element was accumulated most in the scales. The lead (Pb) values in the muscle tissue, the main tissue of concern, were the lowest (0.19 ± 0.05). However, this value is at the threshold of the WHO permissible level of 0.2 µg g^{-1} indicating that in the near future this value could be exceeded unless measures are taken to identify its source and reduce it.

In order to determine the concentrations of the trace elements from these foodstuffs that would actually be assimilated in the body, it will be necessary to determine the trace element levels in the amount of food that is actually ingested. Once in the digestive system, the amount assimilated will depend, among other factors, on their bioavailability of essential trace elements in typical Kenyan diets.

Table 4. The mean concentration levels of heavy metals (µg/g wet weight) in fish tissues.

Element	Tissue / Organ				
	MT	LV	GL	SK	SC
Fe	5.6±0.5	41.2±7.9	4.4±1.2	5.7±3.4	3.9±0.6
Mn	0.7±0.03	1.4±0.3	1.5±0.7	0.5±0.01	0.7±0.02
Cu	0.40±0.02	0.81±0.05	0.63±0.02	0.64±0.01	0.40±0.05
Zn	4.3±1.2	4.5±0.2	9.2±0.2	4.3±0.3	4.4±0.05
Ni	0.11±0.04	0.3±0.01	0.65±0.01	0.4±0.04	0.37±0.04
Pb	0.19±0.05	0.2±0.05	0.34±0.03	0.50±0.02	0.68±0.05

n = 42, **MT** = Muscle Tissue, **LV** = Liver, **GL** = Gills, **SK** = Skin, and **SC** = Scales

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Sri Lanka

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The Energy Dispersive X-ray Fluorescence (ED-XRF) facility was established in 2001 under the Technical Cooperation project on Development and Utilization of Nuclear Analytical Technology (SRL/2/005). The XRF facility consists of X-ray tube with Mo anode, secondary targets and Si/Li detector coupled with portable inspector MCA and Genie 2000 spectrum acquisition software. Qualitative and Quantitative analysis is being carried out using QXAS-BFP (Backscatter Fundamental Parameter method) for thick samples, QAES (P.Kump, Slovenia) for both intermediate thickness and thin samples.

The EDXRF facility is used for the elemental analysis of soil /sediments samples, plant materials, air filters, alloys and water samples.

The analytical services are provided for research institutions, Universities, Geological and Environmental assessment companies to determine major, minor and trace elements in various materials.

Since 1998 the XRF group has also participated in the IAEA/RCA project on “Isotopes and related techniques to assess Air Pollution”. Currently, three research projects on the application of EDXRF technique in environmental studies are being carried out.

Publications of potential interest to the XRF community

- Operating Manual for GENT sampler, RAS/7/013 - Improved Information about Urban Air Quality Management (RCA), prepared under IAEA contract by Andreas Markwitz, New Zealand, 2004
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